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apparent inexactness of certain chemical analyses, as well as facts in mineralogy which at present are not reconcilable with the laws of atomic proportion ; and would show that, where a deviation from these laws is coexistent with crystalline structure, such deviation may be merely apparent, and the crystalline form in reality dependent upon the presence of a body possessed of a definite atomic constitution.

Dr. C. T. Jackson exhibited a fragment of the Dhurmsala meteorite, which had been presented to the Boston Society of Natural History by the Governor-General of India.

Mr. Safford announced the results of his calculations on the perturbations of Uranus.

Five hundred and second meeting.

January 14, 1862. — MONTHLY MEETING.

The PRESIDENT in the chair.

The Corresponding Secretary read various letters relative to the exchanges of the Academy.

F. H. Storer having declined to serve on the Rumford Committee, Prof. Winlock was chosen to fill the vacancy.

The Report to the United States Government on the Physics and Dynamics of the Mississippi, by Capt. Humphries and Lieut. Abbot, of the U. S. Topographical Engineers, received by the Academy from the authors, was referred to Professor Peirce.

W. P. Dexter communicated the following paper, viz. : —

Remarks upon the Recent Determinations of the Atomic Weight of Antimony.

The atomic weight of antimony has been successively investigated by Berzelius, Kessler, Schneider, H. Rose, myself, and Dumas. Very recently Kessler has revised and repeated his determinations, and arrived at a result which "completely agrees" * with that previously obtained by me. I have hitherto abstained from making any remarks upon these researches, or from entering upon any defence of my own work, from the conviction that a determination of an atomic weight, if correct, would certainly be in the end received, and if incorrect, would as certainly be superseded by a better.

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* "Welches (das Atomgewicht) sich nun nach meinen späteren Versuchen als durchaus ubereinstimmend mit dem von Dexter gefundenen herausstellt." — Pogg. Ann., Bd. CXIII. S. 134.

The equivalent found by Berzelius[*] was 129, when reduced to the scale on which H = 1, and it is remarkable as being the only instance in which a grave error has been detected in the numerous determinations to which he devoted a large part of his life.

Passing over the equivalent of Berzelius, which is now admitted to be altogether too high, the other determinations may be divided into two classes; those of Schneider and H. Rose, which place the equivalent at about 120, and those of Kessler, Dumas, and myself, which give a number not varying much from 122. Kessler claims to have been the first to show the error in the equivalent which had been universally adopted on the authority of Berzelius. His earlier experiments gave 123.58 to 123.84 for the atomic weight.[†]

A few months later appeared the elaborate research of R. Schneider of Berlin.[‡] A native sulphide of antimony, said by him to be free from appreciable quantities of arsenic and the metals by which it is usually accompanied, served as the basis of this work. The sulphide was reduced, at a temperature just sufficient to fuse it, by a slow stream of pure hydrogen. The loss of weight, after applying small corrections for a minute quantity of quartz present, for a portion of the antimony volatilized, and for a trace of sulphur retained by the reduced metal, gave the necessary data for the calculation of the atomic weight.

It is an invidious task, especially for a fellow-laborer, to examine into the causes of error in a work so elaborately and conscientiously executed. The results show, however, and Schneider himself admits the presence of, some constant error, in consequence of which the proportion of antimony in the sulphide seemed to increase regularly with the quantity of material operated upon. So that those determinations gave the highest atomic weight in which the largest quantity of sulphide was employed. I am inclined to think that the error may have arisen in part from the action of the flame upon the glass of the tube in which the reduction was effected. It is stated by Stas,* that "all kinds of glass, when long exposed to a red heat in contact with the flame of alcohol or of gas, lose slowly, but continuously, in weight." This loss would have apparently increased the amount of sulphur in the sulphide, and so have led to a too low valuation of the atomic weight. That this is not the only constant error is shown by the fact that those determinations gave the highest equivalent in which, the quantity of substance being the largest, the glass was longest exposed to the action of the flame.

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[*] Schweigg. Journ., Bd. VI. S. 144, and Bd. XXII. S. 69.

[†] Pogg. Ann., Bd. XCV. S. 204.

[‡] Ibid., Bd. XCVIII. S. 293.

Secondly, these experiments were made with a native sulphide of antimony; their success depended upon its purity, and upon its having the precise atomic constitution attributed to it. On the first of these points we have the opinion of Berzelius, that "native compounds are never sufficiently pure to be used in such researches." † We know by the experience of Dumas, of Erdmann and Marchand, and of Scheerer in the determination of the atomic weights of calcium and magnesium, how difficult it is to detect and make allowance for the presence of minute quantities of foreign bodies; and every one who has worked with antimony will admit that the difficulty in this case is still greater. On the subject of the precise atomic constitution of these native compounds I have long had doubts; and the paper which I recently had the honor of submitting to the Academy shows that they may not be without foundation, even when the body can be obtained in well-defined crystals.

Whatever may be thought of these doubts, which it is indeed easy to raise about the best-executed work, the *fact* of the dependence of the atomic weight in Schneider's experiments upon the quantity of matter operated upon, seems to me sufficient to destroy confidence in his results. I have, accordingly, not calculated the probable error of his determinations; his extreme numbers are 120.08 and 120.53, the mean of eight being 120.3.

Professor Rose's work ‡ was published rather as a confirmation of

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[*] "Sans exception aucune, tout verre chauffé longtemps au rouge dans la flamme de l'alcool ou du gaz éclairant, diminue de poids lentement, mais constamment." — Recherches sur les Rapports Réciproques des Poids Atomiques, (Bruxelles, 1860,) p. 17.

[†] "Les composés naturels ne sont jamais assez purs pour être propres à des pareilles recherches." — Traité de Chimie, (Paris, 1847,) Tom. IV. p. 529.

[‡] Pogg. Ann., Bd. XCVIII. S. 455.

the equivalent obtained by Schneider, than as an independent research upon the atomic weight. He gives as trustworthy the result of but one analysis of the chloride, and that not made by himself. From this he derived the number 120.7.

Of the researches which place the atomic weight at about 122, my own * was the first in point of time, and was commenced before the publication of that of Schneider. After attempting without success to deduce the atomic weight from the quantity of gold which a known weight of antimony could precipitate, with the view of rendering as small as possible the influence of the errors of the operation upon the result, the determination was finally effected by oxidizing the pure metal by nitric acid, and ascertaining the weight of the resulting antimoniate of oxide of antimony. That this body has really the composition SbO_4 was also proved by a separate experiment. The process, besides its simplicity and accuracy, has the advantage of giving the atomic weight directly dependent upon that of oxygen. In ten determinations the equivalent was found from 122.24 to 122.48. The most probable value is 122.33; and the probable error of the individual determinations is 0.05.

In the last edition of the *Handwörterbuch der Chemie* † this determination is spoken of as being not so accuräte (*weniger genau*), by which is probably meant that it is not so correct, as that of Schneider. As no reason whatever is given for this opinion, I do not think it calls for any other remark than that the writer, H. Bolley, apparently had not read the paper which he thus criticises. For in the very next article,‡ by the same writer, the determination of chloride of antimony by means of the double chloride of gold and potassium is recommended; although this process had been thoroughly tried by me, in the hope of making it available in the determination of the atomic weight, and stated to lead to completely erroneous results. That this process had given Professor Rose apparently satisfactory results when the equivalent of antimony was taken at 129, would not *generally* be thought a good reason for supposing that it would give equally good ones when the equivalent was found to be only 120. In fact, Rose has since admitted in a similar case, and referring to my experiments, that the process must be abandoned. §

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* Pogg. Ann., Bd. C. S. 563.

† Braunschweig, 1858. Art. *Antimon.*, Bd. II. S. 43.

‡ Art. *Antimon.*, *Bestimmung und Trennung*, S. 56.

§ Pogg. Ann., Bd. CX. S. 541.

In another article of the same work, the objection is raised that "the antimoniate of oxide of antimony (SbO_4) always contains excess of oxide."[*] This is, so far as I know, mere assertion, utterly unsupported by facts. On the contrary, it is stated in another article of the same volume of the same work,[†] that the body in question is obtained in a state of purity by "ignition of nitrate of antimony or of antimonic acid"; that is, by the very operation by which it was obtained in the determination of the atomic weight. The origin of this assertion may, I think, be traced to a passage in Schneider's paper,[‡] in which he says that "there is no proof that this substance (SbO_4) does not give off oxygen when strongly ignited"; and that to this cause may perhaps be ascribed the difference in the results of the earlier and the later determinations of Berzelius. But Schneider made no experiments himself to prove that it *does* give off oxygen, and it is not probable that, were this the case, the fact would have remained unobserved by Berzelius.[§]

Opposed to these unsupported assertions we have the general experience of chemists, and the high authority of Bunsen in particular, who declares that "the best way of determining antimony is as antimoniate of oxide of antimony, since this body is neither volatilized nor decomposed by ignition in contact with air."[‖] Finally, it was shown by me, by direct experiment, that the product of the action of nitric acid upon metallic antimony has, after having been ignited, the composition of antimoniate of oxide of antimony, viz. SbO_4 or Sb_2O_8. The difference between the composition calculated upon this formula and that actually found was such as to indicate an error in the analysis somewhat smaller than the probable error of the individual determinations of the atomic weight.*

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[*] "Doch scheint ein Ueberschuss von Antimonoxyd bei dem antimonsauren Antimonoxyd kaum zu vermeiden." — Art. *Atomgewichte*, S. 473.

[†] Art. *Antimonige Säure,* S. 73.

[‡] *Loc. cit.*, S. 294.

[§] The difference in his results was attributed by Berzelius himself to the fact that his earlier experiments were conducted in vessels of glass, which were incapable of supporting the temperature required for the complete conversion of SbO_5 into SbO_4.

[‖] "Was zunächst die Bestimmung des Antimons anbelangt, so wägt man dasselbe am zweckmässigsten als antimonsaures Antimonoxyd, Sb_2O_8, indem diese Oxydations stufe bei dem Glühen an der Luft weder flüchtig noch zersetzbar ist." — *Unterscheidung und Trennuny des Arseniks vom Antimon und Zinn,* Ann. d. Chem. u. Phys., Bd. CVI. S. 3.

In the research of M. Dumas,† a known weight of chloride of antimony ($SbCl_3$) was dissolved in a solution of tartaric acid, and the quantity of silver required for the exact precipitation of the chlorine determined by volumetric process. Four determinations, said to have

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* Pogg. Ann., Bd. C. S. 577. An abstract of the memoir referred to is appended.

Determination of the Atomic Weight of Antimony. By W. P. Dexter.

(Translated and abridged from the original Memoir in Poggendorff's Annals.)

The antimony used in the following determinations was prepared by igniting commercial tartrate of antimony and potash, which had been previously purified by recrystallization, with an equal weight of nitre, adding to the mass after it had become perfectly white a quantity of hydrate of potash equal to half that of the nitre employed, and keeping the mixture in fusion at a dull red heat for about half an hour. The fused mass was then poured into a clean iron vessel: it dissolved easily and completely in hot water. The solution was filtered, and precipitated as metantimoniate of soda by a solution of common salt, from which the magnesia which it always contains had been separated by means of carbonate of soda. The metantimoniate of soda was washed first by decantation, and then upon a filter. It was then digested with nitric acid to remove the soda, and finally repeatedly washed, by decantation, with dilute nitric acid.

The hydrated antimonic acid was dried and reduced to the metallic state by ignition in a porcelain crucible thickly coated with charcoal. To make sure that the metal should take up no impurities from the charcoal, the latter was used in the state of lampblack, deposited by a lamp fed with oil of turpentine and burning under a large porcelain vessel filled with water. The coal thus obtained is absolutely free from all inorganic impurities, and burns without leaving the slightest trace of ash.

The antimony procured by this process contained sodium, reduced with it from some of the soda which had resisted the action of the nitric acid. It was finely powdered, mixed intimately with a fresh portion of antimonic acid, and again ignited in a porcelain crucible. The metal collected in a button at the bottom covered with a layer of fused oxide of antimony.

The atomic weight having been determined upon one portion of this antimony, the residue was again fused in the same way with more antimonic acid, and another determination made upon the product. The agreement of the two determinations showed that the sodium had been completely removed by the first fusion.

As it was possible that the metal might retain oxide of antimony in combination, a third determination was made upon a portion which had been kept in fusion for half an hour in a current of dry hydrogen. The result, however, was not sensibly altered by this treatment.

The determination of the atomic weight was effected by oxidizing the metal with nitric acid, and converting the residue, by ignition, into the compound of antimonic acid and oxide of antimony expressed by the formula SbO_4 or Sb_2O_8. This pro-

† Ann. Chim. Phys., 3^{me} Série, Tom. LV. p. 175.

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cess has the advantages of simplicity in execution, and of giving the atomic weight directly dependent upon that of oxygen; but in consequence of the high equivalent of antimony the result is very much affected by the unavoidable errors of the operation. This will appear when we consider that the atomic weight is connected with the observed values by the equation

$$Sb = \frac{32\,p}{q-p},$$

in which p denotes the weight of metallic antimony taken, q that of the SbO_4 obtained, and the atomic weight of hydrogen is taken as unity.

If we suppose that the whole error of the operation lay in the determination of q, and differentiate the above equation in respect to this value, we have

$$d\,Sb = -\frac{32\,p}{(q-p)^2}\,dq = -\frac{Sb^2}{32\,p}\,dq;$$

and putting for Sb the value deduced from the determinations, viz. 122.34, and for p the number belonging to any one of these determinations, for example 3, we find that

$$d\,Sb = -156\,dq;$$

or, that in this case a small error committed in the determination of q is multiplied about 156 times in its effect upon the atomic weight, and that this effect increases as the square of the atomic weight to be determined.

These considerations led to many trials of the possibility of deducing the atomic weight from the quantity of gold which a known quantity of antimony could precipitate from an acid solution of the double chloride of gold and potassium ($AuCl_3, KCl$). These attempts proved unsuccessful; the quantity of gold precipitated seemed to be dependent upon the amount of acid in the gold solution, being greatest when the solution contained the least free acid. They showed that this process, which has been recommended for the quantitative analysis of mixtures of SbO_5 and SbO_3 is entirely unreliable. It was noticed that a solution of $SbCl_3$ in hydrochloric acid which had been digested with metallic antimony until it no longer gave a blue color with starch and iodide of potassium, acquired this property after having been exposed for some hours to the action of the air. It would seem that absorption of oxygen takes place with formation of antimonic acid, or the corresponding perchloride of antimony. A similar absorption of oxygen by the salts of arsenious acid has been observed by Fresenius.*

The nitric acid employed for the oxidation of the antimony was most carefully prepared from distilled sulphuric acid, and the purest nitre of commerce from which every trace of chlorine was removed by means of nitrate of silver. It was still further purified by a second distillation from the same nitre, conducted at a temperature below the boiling-point of the acid, in order to prevent the possibility of any solid matter being carried over mechanically with the vapor. The acid thus ob-

* Ann. d. Ch. u. Pharm., Bd. XCIII. S. 384.

been made with pure material, gave the numbers 122, 122, 122.20, and 121.94. The most probable value is 122.07, and the probable

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tained was not perfectly pure, but left, when evaporated, a slight residue, probably arising from its action upon the glass of the retort. The amount of this residue was ascertained, and allowance made for it in the estimation of the weight of the SbO_4. The balance upon which the weighings were made was from Oertling in Berlin, and was used for no other purpose during the work. The weighings were always effected by placing a brass weight of 50 grammes in one pan, while the platinum crucible to be weighed was placed in the other, and brought into equilibrium with it by the addition of weights. The weights were made by Staudinger of Giessen expressly for this purpose; they were entirely of platinum, from 10 grammes downwards, and so accurately adjusted, that, although the balance indicated the 0.00005 of a gramme, not the slightest discrepancy could be observed in comparing different combinations of equal value.

To prevent loss by effervescence in the action of the acid, the platinum crucible was provided with an arrangement consisting of a perforated plate of platinum fitting the inside of the crucible, and having attached to it at some little distance a concentric disk of the same metal, and of greater diameter than the perforation in the plate.

The antimony was reduced to the finest powder in an agate mortar, and acted upon at first with a somewhat diluted acid, in order to prevent a too violent effervescence. But as the product then was chiefly nitrate of oxide of antimony, and it was possible, although not probable, that, if ignited in this state, a portion of the oxide might be volatilized, it was subsequently treated with concentrated acid, to convert it as fully as possible into antimonic acid, and evaporated in an air-bath to dryness.

To protect the contents of the crucible during the ignition from the reducing action of the flame, it was inserted in a hole in the centre of a plate of sheet-iron, a tightly fitting ring of platinum having been interposed between the crucible and the iron.* Of 14 determinations, 4 were rejected as unreliable; the results of the remaining 10 are exhibited in the following table.

		Sb taken.	SbO_4 obtained.	Atomic Weight (O = 100).	Atomic Weight (H = 1).
2	*a*	1.7638	2.2251	1529.4	122.352
3	*b*	1.5909	2.0069	1529.7	122.376
4	*a*	3.0640	3.8660	1528.2	122.256
5	*c*	3.2896	4.1501	1529.2	122.336
7	*d*	1.7488	2.2066	1528.0	122.240
8	*d*	1.5186	1.9157	1529.7	122.376
9	*d*	3.1330	3.9526	1529.0	122.320
12	*b*	1.50265	1.89585	1528.6	122.288
13	*a*	2.0759	2.61825	1531.0	122.48
14	*e*	1.7944	2.26355	1529.9	122.392

The letters *a*, *b*, *c* in the second column denote three different preparations of

* For a more detailed description of the apparatus I must refer to the original paper.

error of the individual observations is 0.1, or twice that of my own determinations. No account is given of the process by which the

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antimony; *d* was formed by a second fusion of *c* with antimonic acid; *e* by fusion in a current of hydrogen.

The probable value of the atomic weight deduced from the ten observations by the method of least squares is 1529.2 for $O = 100$, or 122.336 for $H = 1$; with a probable error, in the individual determinations, of 0.6 in the one case, and of 0.048 in the other. This error corresponds to an error in the operation somewhat less than 0.0003 gramme.

For the composition of the antimoniate of oxide of antimony the probable value is

Sb	79.266
4 O	20.734
	100.

It remains now to be shown, that in the antimoniate of oxide of antimony the antimony and oxigen exist in the exact proportion of 1 atom to 4, as has been assumed in the foregoing calculations.

This composition was inferred by Berzelius from his experiments upon the sulphide; it seemed to me desirable that it should be proved by direct examination of the oxides. For this purpose the oxide precipitated from chloride of antimony by carbonate of potash or soda, which always retains traces of the alkali, was placed in a small platinum boat in a combustion tube, and a stream of dry carbonic acid, generated in a self-regulating apparatus, led through the tube, till the air was completely expelled. The part of the tube in which the oxide lay being heated by a lamp-furnace, the oxide melted, and sublimed in beautiful and perfect crystals, shooting across and filling up the tube. 1.52045 gr. of these crystals, which were proved to be entirely free from any higher oxide of antimony, gave by oxidation with nitric acid 1.60385 gr. SbO_4: consequently 100 SbO_4 may be regarded as containing 94.8 SbO_3. We have before found that 100 SbO_4 contain 79.266 Sb; hence the relation of the oxygen of SbO_4 to that of SbO_3 is that of 100 — 79.266 to 94.8 — 79.266, or of 4.004 to 3.*

It may be stated, then, as the result of this work: —

1. That oxide of antimony cannot be determined quantitatively, as has been asserted, by means of the double chloride of gold and potassium.

2. That solution of chloride of antimony, after having been exposed to the action of the air, will be found to contain a higher degree of oxidation of the metal.

3. That the relation of the oxygen in the oxide, and in the antimoniate of the oxide of antimony, as shown by direct analysis of these oxides, is that of 3 : 4; as has been hitherto assumed.

4. That the probable value of the atomic weight deduced from ten observations is 122.34; the atomic weight of hydrogen being taken as unity.

* If, conversely, the above experiment be used for the determination of the atomic weight, it gives the number 121.84. But it is evidently unsuited to secure any degeee of accuracy; for we have only to admit an error in the operation of 0.00025, that is, less than the probable error of the former observations, to derive from it the same number, 122.34.

chloride was obtained, except that it was prepared with "very pure antimony and dry chlorine, and distilled several times over finely powdered antimony." We have, consequently, no guaranty for its purity beyond the assertion of the author. But this is a point upon which we are entitled to demand the most precise information in a work which claims not only to be an exact determination of a chemical constant, but also to decide the question whether the equivalents are or are not multiples of that of hydrogen. It is well known that upon this very point, the purity of the antimony obtained by a certain process, there was for a long time a disagreement between chemists as eminent as Berzelius and Liebig; and that it was finally conceded that the metal so prepared does contain an appreciable quantity of arsenic. Now what proof have we that the antimony used in these determinations may not have been prepared by the process of Liebig? and that the trifling differences in the results of M. Dumas and myself may not have been caused by the presence of a minute quantity of arsenic, a substance difficult of detection when mingled with a large amount of antimony, and whose atomic weight is lower than that of antimony in the proportion nearly of 3 to 5? If it be considered unfair to M. Dumas to assume that his material was impure, it is certainly fair to demand that he should give the proof that it was not.

The properties of the chloride of antimony, also, are such as to render extreme accuracy difficult of attainment. A body which attracts moisture with the utmost avidity, and which, if every trace of moisture be not excluded, gives on distillation a product containing free hydrochloric acid, is not one which would willingly be selected for the purpose of a normal determination. M. Dumas says that he tried without success to effect the determination by the reduction of the oxide and of the sulphide, and by oxidation of the metal with nitric acid.*

But the last-named process gave Berzelius agreeing results, and I have shown that the accuracy of those obtained by myself in the same way is about twice that of the determinations made upon the chloride. It is not easy to believe that a process which has succeeded in the hands of others would offer any difficulty to so consummate a manipulator as M. Dumas.

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* "J'ai essayé sans succès de déterminer l'équivalent soit en réduisant les fleurs argentines d'antimoine, soit en réduisant le sulfure d'antimoine, soit en acidifiant l'antimoine par l'acide nitrique. Je n'ai obtenu par ces divers procédés que des résultats très-discordants."

An experiment of Mulder[*] deserves notice here, as showing the possible existence of a cause of error in the processes made use of both by Rose and Dumas. Mulder dissolved 1 gramme of silver and 0.13 gr. of antimony in nitric acid, added 5 gr. of tartaric acid to retain the antimony in solution, and then determined the silver by precipitation with a standard solution of salt. He obtained 999.125 instead of 1,000, while a similar experiment without the antimony and tartaric acid gave precisely 1,000 silver. Upon what this difference of nearly 0.9 milligr. depended was not ascertained. It is not impossible that a trace of tartrate of silver may be precipitated with the chloride; and if this be so, the chlorine would be estimated too high, whether determined volumetrically, as in the case of Dumas, or by weight, as was done by Rose; and the atomic weight would consequently be found too low.

It appears from the foregoing remarks that recent investigations may be considered as having led essentially to two different numbers for the atomic weight of antimony. That of these numbers, the one, 120, was first deduced by Schneider, and is supported by a single analysis of Professor Rose. That the other, 122.34 is the result of my own observations, subsequently confirmed by the works of Dumas and of Kessler, of which the first differs only by a few decimals from, and the second agrees precisely with, the equivalent previously obtained by me. I have given the reasons which cause me to doubt the correctness of the equivalent assigned by Schneider; I cannot think that three experimenters, working independently of each other and using different processes, would arrive at results so nearly identical, were these results very far removed from the truth.

Five hundred and third meeting.

January 29, 1862. — STATUTE MEETING.

The PRESIDENT in the chair.

The Corresponding Secretary read a letter of acknowledgment from the Corporation of Brown University for a copy of the Memoirs of the Academy, Vol. VIII. Part I.

Dr. John Dean, of Boston, was elected a Fellow, in Class II. Section 2.

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[*] Die Silber-Probirmethode, von G. J. Mulder, (Leipzig, 1859,) S. 165.